A Reversible Oxidation-Reduction Indicator
of High Potential
Especially Adapted to Oxidimetric Titrations

BY

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INTRODUCTION

There are those in the field of analytical chemistry who believe that major advances in the future must be brought about by the introduction of methods radically different from those in vogue at present. That this may be true does not preclude the development of improvements in existing technique either by means of new reagents or otherwise.

Quantitative analysis as it exists at present makes extensive use of volumetric procedures. Furthermore, an examination of such procedures will quickly reveal the important position occupied by oxidation-reduction methods.

In this thesis there will be described an oxidation-reduction indicator which is reversible and mobile and in short comparable to the common acid-base indicators such as phenolphthalein. This is the first indicator to be described which has these properties and possesses the high oxidation potential necessary for many titrations with strong oxidizing agents. The need for such an indicator becomes apparent after even a casual reading of the literature. Of all the oxidants known potassium permanganate and iodine are most frequently employed, obviously for the sole reason that potassium permanganate by itself and iodine with starch are their own indicators.

Morse and his co-workers [1] showed that manganese dioxide, if present in potassium permanganate solutions, acts as a catalyst in the decomposition of the permanganate and pointed out the precautions necessary in order to prepare a stable solution. Since that time many standard oxidimetric procedures have been based on the use of this reagent. The fact that potassium permanganate does function as its own indicator has been sufficient in the past to outweigh certain drawbacks connected with its use and to give it preference over other powerful oxidizing agents. Potassium permanganate cannot be obtained in a sufficiently high state of purity to make possible direct weighing as a means of standardization. The precautions which must be taken in the preparation of a standard permanganate solution are so well known that they need not be mentioned in detail here. Even with these precautions it is impossible to be sure that the value of the solution will remain unchanged on standing, and re-standardization from time to time is necessary. The reduction product of $KMnO_4$ depends on the acidity of the solution being titrated and it is necessary to so control the conditions that only one product is obtained.

If chloride ion is present, it is oxidized by the permanganate and the result is a fictitious value for the substance being determined. Potassium permanganate is most often used for the determination of iron and many iron ores dissolve best in hydrochloric acid. Hence after solution of the ore it is necessary to remove the hydrochloric acid or to find some method for avoiding its reducing action on the permanganate ion. Furthermore, stannous chloride is one of the reducing agents commonly used to reduce the iron to the ferrous condition prior to titration. If it is desired to titrate with potassium permanganate after solution and reduction with hydrochloric acid and stannous chloride, it is necessary to add the so-called preventive solution. Even then the end-point is a fleeting one. It may also be pointed out that permanganate is not satisfactory if a solution much below 0.02 M. is used on account of the difficulty of judging the end-point.

As everyone knows potassium permanganate is not the only powerful oxidizing agent which the chemist has at his disposal for the quantitative oxidation of active reducing agents. Potassium dichromate and ceric sulfate in particular, deserve consideration. The reduction of dichromate ion is similar to that of permanganate in that it involves more than a simple transfer of electrons. This substance possesses certain advantages over permanganate however. It is relatively more stable and may be obtained in a state of uniform purity. Vosburgh [2] has shown that potassium dichromate recrystallized and either fused, or dried for several hours at 160°, is a satisfactory primary standard. Thus it is possible to prepare a standard solution by direct weighing. Furthermore, the solution is relatively stable. Dichromate does not oxidize chloride ion, at least in the concentrations usually involved in quantitative procedures, and therefore may be used for the titration of iron and other reducing agents in the presence of chloride ion. This makes possible the solution and reduction of iron ores by means of hydrochloric acid and stannous chloride and the subsequent titration with dichromate without the addition of the preventive solution. Some attempts to find suitable inside indicators for use with it will be referred to in a later paragraph. Before the work of Morse (loc. cit.) indicated the proper method of preparing permanganate solutions, potassium dichromate was used in conjunction with the spot-plate and an outside indicator.

Although the possibility of using ceric sulfate as a volumetric oxidizing agent seems to have been recognized for many years, it is only recently that this substance has been investigated in a serious and systematic manner. Willard and Young [3] and Furman and his co-workers [4] have carried out two independent and extensive series of investigations dealing with the quantitative applications of ceric sulfate. By means of poten-

tiometric methods they have shown that it is capable of many of the oxidations for which potassium permanganate is commonly used and in general that it possesses superior qualities as an oxidant. Solutions are easily prepared by heating ceric oxide with excess sulfuric acid. Such solutions, 0.5-1 M with respect to sulfuric acid are extremely stable. Furman showed that they maintain their value for periods up to three months. Willard and Young found that 0.05 N or 0.1 N solutions of ceric sulfate in 0.5 or 1 M sulfuric acid remain stable for as long as forty weeks, even when the stock bottles were opened a number of times during that period. Willard and Young also proved that a solution of ceric sulfate in sulfuric acid is stable on boiling for as long as five hours, or if the solution contains nitric or perchloric acid in addition to the sulfuric acid, for one hour. Kunz [5] has shown that the normal oxidation potential is high (1.44 volts). The reaction for the reduction is a simple and reversible one $Ce^{++++} + e = Ce^{+++}$. It is a reagent which can be used as an oxidizing agent in solutions where a relatively high concentration of chloride ion is present. In this connection Willard and Young showed that potentiometric titrations of ferrous iron in hydrochloric acid are entirely satisfactory, but if the ceric sulfate is diluted with hydrochloric acid prior to titration with ferrous sulfate, the reducing action of the chloride ion on the ceric ion becomes evident.

Unless and until a suitable indicator is found for use with potassium dichromate and ceric sulfate, those who desire to use these excellent oxidizing agents must resort to potentiometric methods for determining the end-point. The potentiometer is a valuable tool—that fact cannot be questioned—but valuable as it undoubtedly is, at the same time it is cumbersome and expensive. The practical analyst prefers to employ a colorimetric indication of the end-point whenever it is possible to obtain the desired degree of precision and accuracy by so doing. This being the case, it is self-evident, that without a satisfactory oxidimetric indicator, neither potassium dichromate nor ceric sulfate will attain the widespread use which might be expected of such valuable reagents.

In acidimetry the problem of the indicator was of necessity met in the beginning and in that field many dye-stuffs have been found to possess the qualifications which enable them to be used as reliable indicators at various pH values over practically the entire range from pH 1 to pH 12.

Until now little progress has been made in this direction in oxidimetry probably because reversible and mobile oxidation-reduction systems are relatively rare whereas reversible and mobile acid-base systems are the rule. Some investigators however have realized the advantages accruing if indicators could be discovered which would increase the availability of oxidants other than potassium permanganate. Their attempts to find

indicators suitable for the purpose have dealt principally with complex organic systems in which the oxidation or reduction reaction is complicated and sluggish. None of these compounds have come into general use.

The author has investigated certain compounds of an entirely different type, namely, certain substituted metal ammines in which the reaction is due merely to the oxidation or reduction of the metallic part of the complex. He has found that the ferrous ortho-phenanthroline complex ion is an excellent oxidimetric indicator, ideally suited for oxidations with ceric sulfate or potassium dichromate in the cold and free from the inherent disadvantages of the previously proposed purely organic indicators. This complex and the similar dipyridyl complex were discovered over forty years ago by Blau [6] and are standard substances to those interested in complex chemistry. Strangely enough, no one has previously thought of investigating their possibilities as indicators for oxidation-reduction reactions.

The first inside indicator proposed for oxidimetric titrations seems to have been diphenylcarbazide. Brandt [7] and Barneby and Wilson [8] proposed the use of this substance which gives a red color in the presence of ferric salts formed in the titration but is colorless in the presence of excess dichromate. Knop [9] introduced diphenylamine as an indicator in the dichromate-ferrous titration. This substance is colorless in the presence of ferrous salts but the first excess drop of dichromate forms an intense violet-blue coloration according to Knop. Knop was able to obtain good agreement with permanganate titrations, and reported that manganese, zinc, aluminum, nickel, cobalt and chromium did not interfere. Diphenlyamine has probably received more attention than any other oxidimetric indicator to date. Sarver [10] after two years' experience with diphenylamine thought that Knop was much too extravagant in his claims. He (Sarver) found that both shade and intensity of color sometimes varied greatly for no apparent reason with resultant danger of overstepping the end-point and permanently oxidizing some of the indicator. Kolthoff and Sarver [11] later made a physico-chemical study of the substance and concluded that it is not a very satisfactory indicator from the stoichiometric point of view because of the possible occurence of side reactions, because of the slight solubility of the intermediate oxidation products diphenyl-benzidine and diphenybenzidine green and because of the instability of diphenylbenzidine violet, the colored oxidation product upon which the indicator property depends. The normal oxidation potential of diphenyl-amine has not been reported. Probably it is impossible to determine with any accuracy because of the irreversibility of one or more of the reactions undergone. From the data of Schollenberger [12] it seems clear that the potential at which the end-point color change is observed is approximately

0.78 volts. As Schollenberger points out, unless the oxidation potential in a solution of ferric and ferrous ions is lowered by the addition of hydrofluoric acid or phosphoric acid, the potential of the system reaches 0.78 volts and hence the end-point color change takes place before quantitative oxidation of the iron occurs. It seems fair to conclude that this indicator is not truly reversible on account of side reactions and decompositions, and that the potential at which the color change occurs is not well suited for many titrations in which potassium dichromate or ceric sulfate may be used.

Clark [13] and his co-workers have investigated a large number of dyestuffs and give the normal oxidation potentials which they found. He is interested primarily in bio-chemical applications and his studies have been made at low hydrogen ion concentrations. In all cases the normal oxidation potentials are too low to be of much value for reactions considered here. The same thing applies to eight dyes reported on by Rapkine, Struyk and Wurmser [14] and to three studied by Michaelis and Eagle.[15] It should be noted also that the use of all these indicators is complicated by the fact that the potential is a function of the hydrogen ion concentration as well as of the oxidant-reductant ratio. Sarver and Kolthoff [16] have investigated diphenylamine sulfonic acid. Its color change is sharper than that of diphenylamine and takes place at a somewhat higher potential (at 0.83-0.84 volts in sulfuric acid solutions) but one which is still low for iron titrations unless phosphoric acid is present. Furthermore, the mechanism of the oxidation is similar to that of diphenylamine and it seems to be no more reversible than is diphenylamine. Knop [17] has tested a number of dyes of the triarylmethane group and has found twelve with a color change at a suitable potential. However, it seems plain that these compounds are not really reversible except possibly within a very short time since the oxidized form is rather rapidly decomposed by powerful oxidizing agents. For this reason they are not likely to prove useful. The necessity of investigating such unsuitable compounds serves to emphasize the need of an indicator which will be truly reversible and mobile.

Properties of an Ideal Oxidation-Reduction Indicator. For purposes of this discussion it is to be understood that reference is had to the case in which the indicator that is added is oxidized or reduced and the oxidized form (I_{Ox}) has a color quite unlike that of the reduced form (I_{Red}). In this case the action of the indicator system does not depend on the specific nature of the oxidant or reductant being titrated but rather on the relative positions of the oxidation potentials of the indicator system and of the system being titrated.

If the reaction of the indicator is written

$$I_{Ox} + e = I_{Red} \quad \text{then,}$$

$$E = E_o + 0.059 \log \frac{I_{Ox}}{I_{Red}} \quad (25^0) *$$

and the color of the indicator in a solution is determined by the ratio $\dfrac{I_{Ox}}{I_{Red}}$.

An indicator may belong to the two-color type or to the one-color type. In the case of a two-color indicator it will be realized that in titrating with an oxidizing agent there must be formed a measurable amount of I_{Ox} in order to recognize a change from the color of the pure I_{Red}. If it is assumed that the change is visible when approximately 10% of the indicator is oxidized then the ratio $\dfrac{I_{Ox}}{I_{Red}} = \frac{1}{10}$ and

$$E = E_o + 0.059 \log 0.1 \quad (25^0)$$
$$\text{or } E = E_o - 0.059$$

(when the indicator reaction corresponds to the equation $I_{Ox} + e = I_{Red}$)

Conversely in titrating with a reductant a measurable amount of I_{Red} must be formed for recognition of color change. Assuming that about one-tenth of the indicator must be reduced the ratio $\dfrac{I_{Ox}}{I_{Red}} = 10$ and

$$E = E_o + 0.059 \log 10$$
$$= E_o + 0.059$$

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* Throughout this paper such equations as this are written with the oxidant in the numerator, and the convention as to sign is that a positive sign indicates an electrode more positive than the solution.

The difference between the two points is approximately 0.12 volts. If it happens that the indicator reaction corresponds to the equation $I_{Ox} + ne = I_{Red}$ the oxidation potentials of those two points would be given by the equation $E = E_o \pm \dfrac{0.059}{n}$.

In the case of a one-color indicator a slightly different situation must must be dealt with. For this discussion it may be assumed that the reduced form is colored and the oxidized form colorless. Assuming further, in titrating with an oxidizing agent, that the color has completely disappeared when approximately 10% of the indicator is still in the reduced form, the ratio $\dfrac{I_{Ox}}{I_{Red}} = 10$. Therefore

$$E = E_o + 0.059 \log 10 = E_o + 0.059 \; (n = 1)$$

In the titration with a reducing agent it would follow that the color of the reduced form would be distinguishable when slightly more than 10% of the indicator had been reduced. If the ratio $\dfrac{I_{Ox}}{I_{Red}} = \dfrac{10}{2}$ instead of $\dfrac{10}{1}$, then

$$E = E_o + 0.059 \log 5 = E_o + 0.041$$

There is a difference of only 0.02 volts between the two points. A similar argument would be employed if the oxidized form is colored and the reduced form colorless. The potential at which it is possible to perceive the change from the original color may be called the effective oxidation potential of the indicator since the potential corresponds to the end-point of the reaction as determined by the indicator.

Next it is necessary to consider the limits within which the effective oxidation potential of the indicator should fall for use in a given titration. In the general case

$$Ox_1 + Red_2 = Red_1 + Ox_2$$

for accuracy of one part per thousand the excess of either Ox_1 or Red_2 at the end-point should be not more than one part per thousand. For excess Ox_1

$$E = E_o + 0.059 \log \dfrac{Ox_1}{Red_2} = E_o + 0.059 \log \dfrac{1}{1000}$$
$$= E_o - 0.177$$

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For excess Red_2

$$E = E_o + 0.059 \log \frac{Ox_2}{Red_2} = E_o + 0.059 \log 1000$$

$$= E_o + 0.177$$

In the titration of Fe^{++} with Ce^{++++}

excess Ce^{++++} $E = E_o - 0.18$ (to the nearest hundredth)

$$(Ce)$$
$$= 1.44 - 0.18$$
$$= 1.26$$

excess Fe^{++} $E = E_o + 0.18$

$$(Fe)$$
$$= 0.75 + 0.18$$
$$= 0.93$$

That is, for an accuracy of one part per 1000 in this titration the effective oxidation potential of the indicator should lie between 0.93 volts and 1.26 volts. The widest use of an indicator with a particular oxidant will be obtained when the effective oxidation potential approaches the upper limit, which, if ceric sulfate is the oxidant is 1.26 volts, since this permits the widest range in normal oxidation potential of the reducing agents which it may be desired to titrate.

In the second place the reaction which the indicator system undergoes should be truly reversible and mobile. When this is not the case, part of the indicator may be irreversibly oxidized (or reduced) by local excess of reagent with the result that the change in color is visible before the equivalence point of the reaction is reached. Since side reactions and decompositions, if they occur, are quite likely to be irreversible, the use of an indicator system subect to these effects should be avoided.

Finally it is axiomatic that the color change of the indicator system should be both vivid and intense if visual observation of the end-point is to be made with the necessary degree of precision. It follows as a corollary to the requirement of vivid and intense color change that the amount of indicator necessary will be small with a resultant small blank correction.

To sum up: An oxidation-reduction indicator for use with a particular oxidant should be a reversible and mobile system with an effective oxidation potential as high as is compatible with the use of that oxidant and with a vivid and intense color change. If we shall be able to find other indicators of lower potential and suitable properties, it will then become

possible to titrate one reducing agent in the presence of another of suffi-
ciently different potential.

Properties of the Blau Compounds. It is well known that there
are many compounds of the type $Me(NH_3)_6X_3$ and $Me(NH_3)_6X_2$ in
which the metal is associated with six molecules of ammonia to form a
positive complex ion, as for example

$$Co(NH_3)_6^{+++}, \ Cr(NH_3)_6^{+++}, \ Co(NH_3)_6^{++}, \ Ni(NH_3)_6^{++}.$$
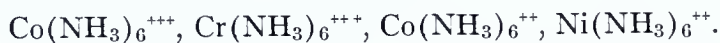
The members of this particular group of metal ammines have been given
the name, hexammine salts. In these hexammines the place of the
ammonia molecules can be taken by other molecules related to ammonia,
for example, pyridine, ethylene diamine, α-α-dipyridyl, o-phenanthroline.

If the equation for the reaction between a metal and ammonia is
written $Me^{++} + 6 \ NH_3 = Me(NH_3)_6^{++}$ (or $(Me^{+++} + 6 \ NH_3 =
Me(NH_3)_6^{+++})$, then application of the law of Chemical Equilibrium
gives

$$\frac{[Me^{++}] \ [NH_3]^6}{[Me(NH_3)_6^{++}]} = K \qquad \left(or \ \frac{[Me^{+++}] \ [NH_3]^6}{[Me(NH_3)_6^{+++}]} = K \right)$$

The stability of these complexes depends on the value of the instability
constant and the rate of the reaction. If it is possible to lower the con-
centration of either the metal ion or the ammonia sufficiently, the com-
plex can be decomposed. As a matter of fact sulfide-ion precipitates the
metal sulfide from the majority of these complexes and so decomposes
them. Ammonia combines with hydrogen ion to form the every stable
ammonium ion:

$$NH_3 + H^+ = NH_4^+$$

Addition of acid to a hexammine ion, therefore, represents a possible
method of reducing the concentration of ammonia. It has been found
that many of the hexammines are decomposed readily by this means.
The reaction is $Me(NH_3)_6^{++} + 6 \ H^+ = Me^{++} + 6 \ NH_4^+$ for a diva-
lent metal. That is, these complexes are less stable than the
ammonium complex. There are exceptions, however, notably the cobaltic
ammonia complex ion $Co(NH_3)_6^{+++}$ which is not decomposed even by
boiling with HCl. When a diamine replaces the ammonia in a complex,
a ring structure is obtained. In general complexes with ring structure
are found to possess a relatively high degree of stability.[18] This is par-
ticularly true of five and six-membered rings. For example, not only

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is the ferrous o-phenanthroline complex unusually stable in the thermodynamic sense, but its decomposition by strong acids is a slow reaction.

Blau (loc. cit.) prepared α-α-dypyridyl by the dry distillation of the copper salt of picolinic acid. He prepared o-phenanthroline from o-phenylene diamine or from o-amino quinoline by the Skraup synthesis. In each case he obtained poor yields.

α-α-dipyridyl   o-phenanthroline
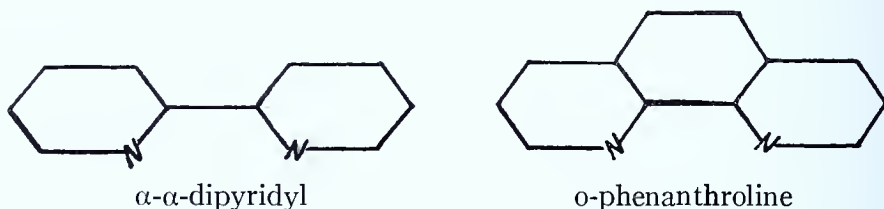
Although difficulty soluble in cold water, Blau found that each compound would react with ferrous sulfate to give a compound extremely soluble and intensely red in color. From these, by salting out with excess of the specific reagent he obtained the slightly less soluble chlorides bromides and iodides. His analysis agreed with the formula $Fe(C_{10}H_8N_2)_3X_2$ for the dipyridyl complexes and $Fe(C_{12}H_8N_2)_3X_2$ for the phenanthroline complexes, where X is a monovalent acid radical. He reported that the presence of alkali and alkaline earth salts, also aluminum, manganese and lead salts did not prevent the formation of the ferrous complexes. Cobalt, nickel, copper, zinc and cadmium salts did prevent their formation if added before the ferrous sulfate bud did not cause decomposition of the ferrous complexes once they were formed. Dilute solutions of the active acids decomposed the ferrous complexes exceedingly slowly in the cold, but more rapidly hot as shown by the following equation for the ferrous phenanthroline complex.

$$Fe(C_{12}H_8N_2)_3^{++} + 6\ H^+ = 3\ C_{12}H_8N_2H_2^{++} + Fe^{++}$$
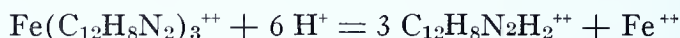
Excess $FeSO_4$ retarded the reaction indicating its reversibility.

Blau found that neither the dipyridyl nor the phenanthroline ferrous complex was oxidized by atmospheric oxygen. Both were oxidized reversibly by more powerful oxidizing agents such as concentrated sulfuric acid, nitric acid, chlorine water, potassium permanganate to a complex of the type $Fe(C_{12}H_8N_2)_3^{+++}$. The solution was blue of less intensity that the red of the reduced form.

Both α-α-dipyridyl and o-phenanthroline have been prepared by others since they were discovered by Blau; dipyridyl has been prepared by Meyer and Hofmann-Meyer [19], by Wibaut [20] and by Hein and Retter [21].

The latter heated a mixture of pyridin and ferric chloride in a bomb tube. Hieber and Muhlbauer [22] prepared phenanthroline from ortho-phenylene diamine using the method of Blau. Smith [23] prepared phenanthroline from o-amino quinoline but not from o-phenylene diamine.

In this investigation it has been found that the ferrous o-phenanthroline complex possesses the properties requisite for an oxidimetric indicator. The reaction

$$Fe(C_{12}H_8N_2)_3^{++} = Fe(C_{12}H_8N_2)_3^{+++} + e \text{ is reversible.}$$

The blue color of $Fe(C_{12}H_8N_2)_3^{+++}$ is so much less intense that the substance functions effectively as a one-color indicator. The color change is vivid and of such intensity that it is satisfactory even in the presence of the color imparted to a solution by chromic and ferric compounds in the presence of HCl when potassium dichromate is used to oxidize a ferrous solution. The substance is not decomposed by powerful oxidizing agents. Even sodium bismuthate has no effect other than the oxidation to the ferric form. It is very stable in either sulfuric acid or hydrochloric acid in the cold. The normal oxidation potential is 1.14 volts and it will be shown later that the effective oxidation potential is approximately 0.06 volts above this. It is capable of a high degree of precision in the oxidation of ferrous iron by either Ceric sulfate or potassium dichromate and should be valuable in the titration of any active reducing agent by either of these oxidants in so far as such titrations may be performed at ordinary temperatures.

EXPERIMENTAL

In the present investigation dipyridyl was prepared by the bomb tube method of Hein and Retter in rather poor yield. The ferrous complex was prepared by dissolving the calculated amounts of the base and ferrous sulfate in water. Preliminary titrations of potassium dichromate with ferrous sulfate indicated that consistent results might be obtained, especially if the indicator were added just before reaching the end-point. If the indicator is added at the beginning of a titration, the color fades considerably before the end-point is reached in acid solution of the concentration used (1.5 M HCl). On this account the ferrous dipyridyl complex is not as satisfactory as the ferrous phenanthroline complex which has proved to be much more stable in acid, and further investigation of this compound was omitted in favor of the phenanthroline complex.

Ortho-phenanthroline was prepared from ortho-phenylene diamine by the Skraup synthesis using arsenic acid as the oxidant as proposed by
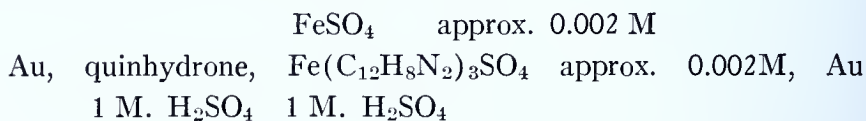
Knuppel.[24] Considerable difficulty was encountered in obtaining a satisfactory yield of pure product. The following procedure was finally arrived at as being the most satisfactory: Mix together 50 grams sulfuric acid approx. 100%, 50 grams glycerine, 20 grams arsenic acid (As_2O_5), heat to 110° and add 10 grams o-phenylene diamine, keep at 140° under reflux for one and one-half hours. Pour reaction mixture into water, make alkaline with sodium hydroxide and allow to stand for two or three days; filter, dry at a low temperature to give a granular product suitable for extraction and extract with boiling benzene. On cooling, the o-phenanthroline crystallizes in a fairly pure state. Vacuum distillation or crystallization from water are suitable methods of purification. Yield about five grams. M. P. 97°. This and other properties are in agreement with those described by Blau.

The solution of the ferrous phenanthroline complex used as indicator in all subsequent experiments was prepared by weighing accurately the calculated amounts of o-phenanthroline hydrate ($C_{12}H_8N_2H_2O$) and ferrous sulfate and dissolving in water to give a solution 0.025 Molar. One drop of this solution was used as the indicator in each titration. With the dropper used, one drop was equivalent to 0.03 c.c. and 0.03 c.c. of 0.025 M indicator is equivalent to less than 0.01 c.c. of 0.1 M reagent. Since this quantity is within the limits of precision of volume burettes no blank correction is necessary.

The ferrous phenanthroline ion is much more stable in acid solution than the corresponding dipyridyl ion. A drop of the former in 200 c.c. of 1 M H_2SO_4 at room temperature undergoes no visible change in color intensity during a period of hours. The same applies to HCl solution. Titrations may be carried out at 30° with complete satisfaction. At 60° however the color fades in a very few minutes.

Determination of Normal Oxidation Potential of Ferrous ortho-Phenanthroline Sulfate. A mixture of ferrous sulfate and ferrous phenanthroline sulfate was titrated potentiometrically with ceric sulfate using a quinhydrone reference electrode, the electromotive force was plotted against titer and the normal oxidation potential of ferrous phenanthroline sulfate calculated from fixed points on the curve. The cell studied may be represented as follows:

$$FeSO_4 \quad approx.\ 0.002\ M$$

$$Au,\quad quinhydrone,\quad Fe(C_{12}H_8N_2)_3SO_4 \quad approx.\quad 0.002M,\quad Au$$
$$1\ M.\ H_2SO_4 \quad 1\ M.\ H_2SO_4$$

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The quinhydrone was triturated with 1 M. H_2SO_4 immediately before use in the half-cell. It was connected with the other half-cell by means of a 1 M. H_2SO_4 salt-bridge. To minimize loss through diffusion of the solution being titrated, the end of the salt bridge dipping in this solution was closed by a glass plug coarsely ground. The concentration of the $Ce(SO_4)_2$ solution used for titration was 0.01M and it was 1M with respect to H_2SO_4. 0.119 g. of phenanthroline and 0.06 of ferrous sulfate were dissolved in 50 c.c. water. To insure the absence of excess ferrous ion from this solution a gram of sodium carbonate was added, air drawn through for an hour, and the resultant ferric hydroxide removed by filtration. This solution was mixed with a solution of 0.06 g. of ferrous sulfate dissolved in 1 M H_2SO_4 which had been previously drawn through a Jones Reductor. The whole was made up to 200 c.c. 1 M with respect to H_2SO_4 and titrated at once with 0.01 M $Ce(SO_4)_2$.

Results of one such titration are shown in Table No. 1, and the curve obtained by plotting E. M. F. against titer is shown in Fig. No. 1.

TABLE NO. 1

Potentiometric titration of a mixture of ferrous sulfate and ferrous o-phenanthroline sulfate with ceric sulfate

Total $Ce(SO_4)_2$	E. M. F. volts	Total $Ce(SO_4)_2$	E. M. F. volts
0.00	-0.179	26.0	0.306
2.0	-0.102	29.0	0.340
4.0	-0.073	32.0	0.360
6.0	-0.057	35.0	0.379
10.0	-0.033	38.0	0.403
15.0	-0.005	40.0	0.432
20.0	+0.026	40.5	0.447
22.0	0.041	40.8	0.461
23.0	0.056	41.0	0.477
24.0	0.110	41.2	0.509
24.2	0.154	41.5	0.518
24.4	0.235	43.0	0.536
24.6	0.254	45.0	0.555
25.0	0.278	82.2	0.655
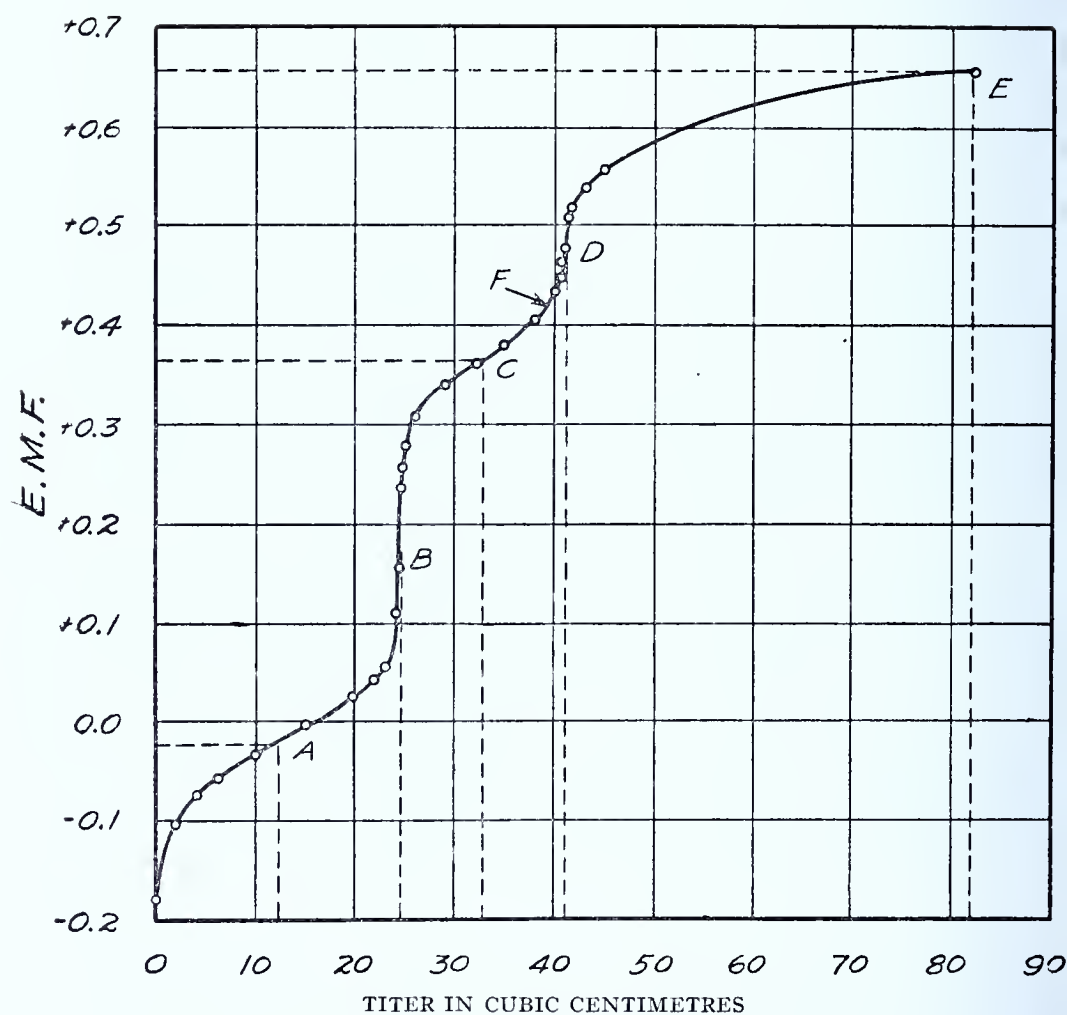
Titration of a solution of ferrous sulphate and ferrous phenanthroline sulphate in 1 M. sulphuric acid with approximately 0.01 M. ceric sulphate in 1 M. sulphuric acid.

Quinhydrone in 1 M. sulphuric acid used as a reference electrode.

There are two well defined points of inflection, B and D (fig. 1). B denotes the complete oxidation of ferrous iron to ferric and D, complete oxidation of the ferrous phenanthroline complex to the ferric phenanthroline complex. A represents the point of half-oxidation of the ferrous sulfate; therefore, the potential at A represents the normal oxidation potential of the ferric-ferrous system. Similarly C represents half-oxidation of the indicator system and the potential at C, the normal oxidation

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potential of the indicator system. The point E was obtained by adding an excess of ceric sulfate equal to the amount required for the reaction; hence, the potential at E is the normal oxidation potential of the ceric-cerous system. The observed value of C (0.36 volts) is 0.38 volts above A (observed, -0.02 volts). But the normal oxidation potential of the ferric-ferrous system against the normal hydrogen electrode is 0.75 volts. (The most recent determination of this value has been reported by Popoff and Kunz [25] who give the above value.) Therefore, the value of C, that is, the normal oxidation potential of the indicator system is 0.75 plus 0.38 or 1.13 volts. Similarly, it may be seen that the observed value of C is 0.29 volts below E, the normal oxidation potential of the ceric-cerous system which, according to Kunz (loc. cit.), is 1.44 volts against the hydrogen gas electrode is one molar sulfuric acid. On this basis, therefore, the normal oxidation potential of the indicator system is 1.44-0.29 which equals 1.15 volts. Good agreement was obtained between two determinations carried out in this manner as will be seen by examining Table 2.

TABLE NO. 2

Normal Oxidation Potential of Indicator System

Calculated from observed value of

	$\dfrac{Fe^{+++}}{Fe^{++}}$ system	$\dfrac{Ce^{++++}}{Ce^{+++}}$ system		mean
1.	1.13 v.	1.15		1.14
2.	1.13 v.	1.14		1.135
			mean	1.14

By making the concentration of the sulfuric the same throughout the cell and making the concentration of ferrous sulfate and ferrous phenanthroline sulfate small in comparison with that of sulfuric acid, the liquid junction potential must be practically negligible. It is not necessary to know the potential of this quinhydrone half-cell relative to the normal hydrogen electrode since the known values for the normal oxidation potentials of the ferric-ferrous and ceric-cerous systems furnish two points of reference once they are established on the curve (Fig. 1).

Effective Oxidation Potential of Ferrous ortho-Phenanthroline Sulfate. In the theoretical discussion of the properties of an ideal indicator the term, effective oxidation potential, was introduced to des-

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ignate the potential which corresponds to the end-point of a reaction as determined by the indicator. The effective oxidation potential of the ferrous phenanthroline system was determined very simply by diluting a small quantity of the indicator solution one hundred times and adding this dilute solution drop by drop to 200 c.c. of one molar sulfuric acid containing 20 c.c. of 0.1 molar ferrous sulfate, these being the quantities frequently employed in the titrations to be described later. The color was not perceptible until after the addition of ten drops of the diluted indicator solution. This amount corresponds to the point reached in a titration where all but 10% of the indicator has been oxidized. From the equation

$$E = E_o + 0.059 \log \frac{I_{Ox}}{I_{Red}} \quad \text{(page 10)}$$
$$= E_o + 0.059 \log 10$$
$$= E_o + 0.059$$

Since E_o for the indicator system is 1.14 volts.
$$E = 1.14 + 0.06 \quad \text{(to nearest hundredth)}$$
$$= 1.20$$

That is, the effective oxidation potential of this indicator system when used in titrations with an oxidizing agent such as ceric sulfate, is approximately 1.20 volts or 0.06 volts above its normal oxidation potential. This is the point marked F in Fig. 1. The value, 1.20 volts, is most satisfactory since it is within 0.06 volts of the limit which has been set for use with ceric sulfate (page 12) if precision of one part per thousand is the aim. It was pointed out previously that the higher the effective oxidation potential of an indicator (within the limits of the particular oxidant) the wider will be its use.

Results Obtained Through the Use of the Ferrous Phenanthroline Complex as an Indicator in Oxidimetric Titrations. In the titrations which are reported in the following paragraphs ferrous ion has been selected as the reducing agent to be used in conjunction with ceric sulfate, potassium dichromate or potassium permanganate. The appropriateness of choosing iron becomes evident from two considerations. First, it is probably determined by oxidimetric means more frequently than any other metal; second, the use of excess standard ferrous sulfate solutions and back titration of the excess with an oxidizing agent is a procedure which is frequently adopted. Furthermore, the reaction with any of the oxidants mentioned is one which takes place smoothly and rapidly at room temperature.

Titrations with Potassium Dichromate as the Oxidant. The potassium dichromate used was first recrystallized and fused as advocated by Vosburgh (loc. cit.). For one series of experiments shown below a 0.017M (0.1N) solution was prepared. For the others a small sample was weighed out for each titration. For each series a ferrous sulfate solution approximately 0.1M. was prepared by dissolving 40 g. of ferrous ammonium sulfate in a liter of 1 M. sulfuric acid. As in all the titrations one drop of indicator solution was used.

In the titration of dichromate with ferrous sulfate in hydrochloric acid solution a yellow-green color is developed as the end-point is approached. At the end-point the addition of less than a drop of reagent is sufficient to develop rapidly a red-orange color. In the reverse titration the change is not as rapid and it is necessary to wait a few seconds between each drop of reagent as the end-point is approached. In spite of the color of the chromic and ferric compounds present one drop of the indicator is sufficient to give a color change which is sharp and easily visible. When sulfuric is the acid used, the color near the end-point becomes blue-green and at the end-point there is a sharp change to a gray-violet. In the titration of ferrous sulfate with dichromate in sulfuric acid it is again necessary to wait a few seconds for the end-point color to be developed.

TABLE NO. 3

Determination of the ratio $\dfrac{K_2Cr_2O_7}{FeSO_4}$

A. 20-30 c.c. portions of $K_2Cr_2O_7$ were diluted with 180 c.c. HCl (conc. shown) and titrated with $FeSO_4$.

B. 20-30 c.c. portions of $FeSO_4$ were diluted with 180 c.c. HCl and titrated with $K_2Cr_2O_7$.

HCl conc.	No. of observations	Ratio $\dfrac{K_2Cr_2O_7}{FeSO_4}$ Mean	Average deviation parts per 1000	Extreme deviation parts per 1000
		A		
2 M.	8	1.0205	0.5	1.7
3 M.	4	1.0205	0.5	1.3
		B		
2 M	8	1.0209	0.4	1.7
3M	4	1.0208	0.4	1.0

Titrations of ferrous sulfate with potassium dichromate as in Table No. 3B, but in the presence of mercuric, aluminum, nickel, ferric or zinc ions show that moderate amounts of these substances have no effect on the titration.

TABLE NO. 4

Determination of Molarity of Ferrous Sulfate Solutions

A. Weighed samples of purified $K_2Cr_2O_7$ (0.10-0.21 grams) were dissolved in 200 c.c. of HCl or H_2SO_4 and titrated with $FeSO_4$.

B. 20-30 c.c. portions of the $FeSO_4$ solutions used in A were diluted to 200 c.c. with 1 M H_2SO_4 and titrated with $KMnO_4$ standardized against Bureau of Standards sodium oxalate in order to compare results with those obtained in A.

FeSO₄ soln. No.	Acid and conc.	No. of obs.	Molarity of FeSO₄ Mean	Average deviation parts per 1000	Extreme deviation parts per 1000
			A		
1.	H_2SO_4 1.5 M.	4	0.09803	0.6	1.7
2.	HCl 2 M.	4	0.09761	0.4	1.4
3.	{HCl 1.5 M.	2	0.09608	0.4	0.4
	}HCl 3 M.	2	0.09609	0.5	1.0
4.	HCl 2 M.	3	0.10170	0.1	0.2
5.	H_2SO_4 2 M.	3	0.09721	0.6	1.7
6.	HCl 2 M.	8	0.10287	0.6	1.9
7.	HCl 2 M.	5	0.09836	0.5	1.3
			B		
1.	H_2SO_4 1 M.	3	0.09809	0.4	1.0
2.	" 1 M.	2	0.09763	0.7	1.3
3.	" 1 M.	2	0.09598	0.7	1.3
4.	" 1 M.	4	0.10169	0.3	0.8

An examination of the data bearing on the titration of potassium dichromate with ferrous sulfate or on the reverse titration indicates that the precision is of a high order and that the accuracy is fully equal to that obtained with potassium permanganate. This is true whether the titration is carried out in sulfuric acid or hydrochloric acid, although it is more satisfactory from consideration of the end-point to work in hydrochloric acid solutions. Results are not affected by changing the hydrochloric acid concentration from 1.5 molar to 3 molar. The results shown in Table 4 are of particular importance for their bearing on the standardization of ceric sulfate solutions which is described later. A comparison of the molarity of ferrous sulfate as determined against potassium dichromate and against sodium oxalate by way of potassium permanganate (solutions 1-4) is highly satisfactory. There is full and complete agreement between the two sets of results. For standardizing ferrous sulfate solutions against potassium

dichromate it is recommended to weigh out 0.10-0.16 grams samples of recrystallized and fused potassium dichromate, dissolve in 200 c.c. two molar hydrochloric acid, add one drop of indicator and titrate with the ferrous sulfate solution.

Titrations with Ceric Sulfate as the Oxidant. The ceric sulfate solutions were prepared from c.p. ceric oxide by treatment with conc. sulfuric acid as described by Willard and Young (loc. cit.). The solutions were approximately 0.1 molar and 1 molar with respect to sulfuric acid. 0.1 molar ferrous sulfate solutions were prepared as described previously. Titrations were carried out under varying conditions as to total initial volume, acid concentration (both hydrochloric acid and sulfuric acid) and volume of ceric sulfate or ferrous sulfate. One drop of the indicator solution was used in each case. In the presence of sulfuric acid the color of the ceric ion disappears before the end-point is reached and the solution is almost colorless. At the end-point the addition of a fraction of a drop of ferrous sulfate solution causes the appearance of the red color of the reduced form of the indicator. In the titration of ferrous sulfate with ceric sulfate the disappearance of the red color is also rapid. From the standpoint of visibility and sharpness the color change at the end-point could hardly be improved upon. In the titration of ferrous sulfate with ceric sulfate in the presence of hydrochloric acid the solution becomes orange as the ferrous iron is oxidized, but there is no interference with the observance of the end-point.

TABLE NO. 5

Determination of the Ratio $\dfrac{Ce(SO_4)_2}{FeSO_4}$

A. 20-25 c.c. of $Ce(SO_4)_2$ solution diluted to 100-300 c.c. with H_2SO_4 and titrated with $FeSO_4$. (45 c.c. $CeSO_4)_2$ in one case.)

B. 20-25 c.c. of $FeSO_4$ diluted to 100-300 c.c. with H_2SO_4 and titrated with $Ce(SO_4)_2$.

C. 20-25 c.c. $FeSO_4$ solution diluted to 100-300 c.c. with HCl (H_2SO_4 in last series for comparison) and titrated with $Ce(SO_4)_2$.

Initial volume c.c.	H_2SO_4 conc.	No. of obs.	Ratio $\dfrac{Ce(SO_4)_2}{FeSO_4}$ Mean	Average deviation parts per 1000	Extreme deviation parts per 1000	Molarity of $Ce(SO_4)_2$ Mean
			A			
200	1 M.	8	0.9725	0.2	0.9	0.09994
200	0.5 M.	2	0.9728	0.1	0.1	0.09993
200	3 M.	2	0.9726	0.3	0.6	0.09994
100	1 M.	2	0.9732	0.3	0.5	0.09988
300	1 M.	2	0.9724	0.4	0.7	0.09995
45 c.c. $Ce(SO_4)_2$						
200	1 M.	2	0.9726	0.5	1.0	0.09994
			B			
200	1 M.	6	1.0558	0.4	1.1	0.09812
200	0.5 M.	2	1.0551	0.2	0.3	0.09820
200	3 M.	2	1.0558	0.8	1.5	0.09813
100	1 M.	2	1.0559	0.4	0.7	0.09813
300	1 M.	2	1.0553	0.0	0.0	0.09818
45 c.c. $FeSO_4$						
200	1 M.	2	1.0557	0.4	0.7	0.09815
Reverse Titration						
200	1 M.	4	1.0558	0.5	1.5	0.09813
			C			
	HCl					
200	1 M.	6	0.9574	0.4	1.5	
200	0.5 M.	2	0.9575	0.3	0.6	
200	3 M.	2	0.9578	0.4	0.7	
100	1 M.	3	0.9574	0.4	1.1	
300	1 M.	3	0.9574	0.6	1.6	
45 c.c. $FeSO_4$						
200	1 M.	3	0.9573	0.5	1.3	
	H_2SO_4					
200	1 M.	4	0.9573	0.3	1.1	

The end-point in these titrations is exceptionally vivid and sharp. It is obvious that the degree of precision is high both in the titration of ferrous sulfate with ceric sulfate and the reverse titration. The results are in complete agreement under a variety of conditions since acid concentration, total volume of solution and amount of reagent being titrated have been varied over a considerable range. It is immaterial whether sulfuric acid or hydrochloric acid is used in the titration of ferrous sulfate with ceric sulfate. In connection with the precision of the above titrations it may be added that the mean of the 18 titrations in series A is 0.9726, the average deviation is 0.3 parts per 1000 and the extreme values are 0.9720 and 0.9734. The other two series are equally satisfactory. The values under the heading, "Molarity of ceric sulfate" will be mentioned in a succeeding section which deals with standardization of ceric sulfate. They were found using the molarity of the ferrous sulfate solution as determined against potassium dichromate.

Ceric-ferrous titrations with weight burettes showed a very striking degree of precision. For the weight titrations a 0.1 molar solution of ferrous sulfate, which was one molar with respect to sulfuric acid, was stored under an atmosphere of carbon dioxide and syphoned into the burette as required. In Series 1 (Table 6) 18-26 grams of ceric sulfate solution were run into 200 c.c. of one molar sulfuric acid and titrated with ferrous sulfate using one drop of indicator. In Series 2 the ferrous sulfate was added rapidly until the end-point was over-stepped and the titration was completed by adding from a volume burette ceric sulfate diluted ten times. The very excellent degree of precision obtained becomes apparent by a glance at Table 6.

TABLE NO. 6

Weight Titrations

Series	No. of obs.	Mean Ratio $\dfrac{Ce(SO_4)_2}{FeSO_4}$	Average deviation parts per 10000	Extreme deviation parts per 10000
1.	6	1.0991	1	3
2.	4	1.0963	1	3

After observing the precision attainable with 0.1 N. reagents the problem of titrations involving 0.01 N. reagents was thought worth investigating and figures illustrative of the results are given in Table No. 7. In the first series 20-40 c.c. of 0.01M. ferrous sulfate in 200 c.c. of 1 M. sulfuric acid were titrated with 0.01 M. ceric sulfate. In the

second series potassium permanganate in conjunction with the indicator was used and in the third series, potassium permanganate without the indicator.

<div align="center">

TABLE NO. 7

Titrations with 0.01 N. Reagents

</div>

Series	Oxidant	No. of obs.	Blank cor. c.c.	Mean Ratio	Average deviation parts per 1000	Extreme deviation parts per 1000
1.	$Ce(So_4)_2$	8	0.08	0.9610	0.6	2
2.	$KMnO_4$	6	0.10	1.071	0.5	2
3.	$KMnO_4$	6	0.26	1.074	1	5

In these cases also it is obvious that the use of the indicator gives concordant results whether ceric sulfate or potassium permanganate is the oxidant. The difficulty of obtaining precise results with 0.002 M. $KMnO_4$ as its own indicator is well-known. Comparison of the results in series 2 and 3 shows that this difficulty is overcome when the end-point is obtained through the agency of the ferrous phenanthroline complex as the indicator.

Standardization of Ceric Sulfate Solutions. Two methods for standardization of ceric sulfate have been investigated by the author and the results compared. (One) Potassium dichromate is used as the primary standard; Ferrous sulfate is standardized against dichromate and this standard solution of ferrous sulfate used at once to standardize the ceric sulfate. (Two) Sodium oxalate is the primary standard; excess ceric sulfate is allowed to react with a solution of sodium oxalate and the excess titrated with ferrous sulfate. For this purpose, it is necessary to know only the ratio between the ceric sulfate and ferrous sulfate.

Potassium Dichromate as the Primary Standard. The author has shown that in the standardization of ferrous sulfate against potassium dichromate a high degree of precision may be obtained, and further that the results are in excellent agreement with those obtained for the same ferrous solution against sodium oxalate by way of potassium permanganate. He has shown also that the degree of precision obtained in the ceric-ferrous titration is of a superior order. It remains then to use the molarity of the ferrous sulfate solution as found by means of dichromate in order to calculate the molarity of the ceric sulfate solution. This has been done and results are in the last column of Table 5 (A and B).

Sodium Oxalate as the Primary Standard. Both Willard and Young and Furman point out that at room temperature the reaction between ceric sulfate and sodium oxalate is so slow that a titration is not feasible. The titration must be carried out at an elevated temperature as is the case with permanganate. At the temperature necessary a titration using the indicator is impossible, since as Blau pointed out, the ferrous o-phenanthroline sulfate reacts with acids at these higher temperatures. Willard and Young (loc. cit.) refer to the stability of ceric sulfate solutions toward heat. Therefore, it seemed that it should be possible to dissolve the oxalate in excess ceric sulfate, heat to that temperature which experiment revealed as the most satisfactory, allow the solution to cool and titrate the excess ceric sulfate with ferrous sulfate. In the investigation of this matter various temperatures were tried from the boiling point down finally to room temperature. The results obtained are shown in Table No. 8.

TABLE NO. 8

Determination of Molarity of Ceric Sulfate against
Sodium Oxalate

A. 50.06 c.c. portions of $Ce(SO_4)_2$ pipetted into beaker, 20 c.c. of 9 M. H_2SO_4 added and sufficient water to make total volume approximately 200 c.c. Oxalate sample (0.12-0.24 grams) added and dissolved completely. Temperature raised to point shown, solution allowed to cool and excess $Ce(SO_4)_2$ titrated with $FeSO_4$ after finding the ratio $\dfrac{Ce(SO_4)_2}{FeSO_4}$. (Same $Ce(SO_4)_2$ solution used for first four series of observations.)

B. 50.06 c.c. $Ce(SO_4)_2$ pipetted into 200 c.c. water and oxalate sample dissolved. Solution allowed to stand for one hour, 20 c.c. $9MH_2SO_4$ added and excess $Ce(SO_4)_2$ titrated with $FeSO_4$.

C. As in B but solutions heated to 40-50° and cooled.

Temp.	No. of obs.	Molarity $Ce(SO_4)_2$ Mean	Average deviation parts per 1000	Extreme deviation parts per 1000
		A		
100°	3	0.09984	0.6	1.9
60°	2	0.09983	0.1	0.1
40°	2	0.09989	0.3	0.5
30°	2	0.09989	0.7	1.8
		B		
Room temp.	8	0.09686	0.5	2.3
		C		
40–45°	9	0.10235	0.4	2.0

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Comparison of values of molarity of ceric sulfate solutions used above and others for which details need not be reported here, as found by different methods. Mean values of two or more determinations given

Solution No.	MOLARITY OF Ce(SO$_4$)$_2$ AGAINST		
	K$_2$Cr$_2$O$_7$ through FeSO$_4$ Na$_2$C$_2$O$_4$	Na$_2$C$_2$O$_4$ Excess Ce(SO$_4$)$_2$ titrated with FeSO$_4$	Na$_2$C$_2$O$_4$ through KMnO$_4$ and FeSO$_4$
1.	0.09857	0.09845	
		0.09852	
2.	0.09994	0.09986	0.09994
3.	0.09814		
	0.09823	0.09819	0.09824
4.	0.09751	0.09751	
5.	0.09776	0.09783	
	0.09784		
6.	0.09678	0.09687	
		0.09682	

The results in the last column of Table 5 (A and B) give the molarity of ceric sulfate solutions as found by means of standard ferrous sulfate. Previous results show that it is immaterial whether the ferrous sulfate is standardized against potassium dichromate or against sodium oxalate by way of permanganate. The precision of these values for the molarity is of the same order as the values for the ratio for which the average deviation and extreme deviation are given.

Recommended procedure: Standardize ferrous sulfate solution as described on page 21. Dilute 20-25 c.c. portions of ceric sulfate solution to 200-250 c.c. with 1 M. sulfuric acid, add one drop of indicator and titrate with the standard ferrous sulfate.

Perhaps the standardization of ceric sulfate by the second method described is to be preferred since by the use of sodium oxalate the determination is more directly related to a primary standard. The results cited in Table 8 indicate that the method is precise whether the reaction between sodium oxalate and excess ceric sulfate is allowed to proceed in the cold or at an elevated temperature. Examination of the results obtained by this and other methods (Table 9) shows that the agreement which exists among the methods used is excellent.

In standardizing ceric sulfate against sodium oxalate it is satisfactory to pipette 50 c.c. ceric sulfate into 150-200 c.c. of 1 molar sulfuric acid

(or into water to which 20 c.c. of 9 molar sulfuric acid is subsequently added); dissolve in this solution 0.12-0.20 grams sodium oxalate; warm to 40-45° and allow to cool, or allow to stand at room temperature for 45-60 minutes; add one drop of indicator and titrate the excess ceric sulfate with ferrous sulfate. It is convenient to determine the ratio $\dfrac{Ce(SO_4)_2}{FeSO_4}$ while the solution is being allowed to cool or stand the required length of time.

With regard to the time the solution should stand, 45 minutes may be somewhat longer than necessary but it seems better to err in that direction than in the opposite. Results in a few cases in which the solutions were titrated immediately after the oxalate had dissolved or within a period of ten to fifteen minutes were found to run slightly high (2 or 3 parts per 1000).

It is highly probable that organic bases closely related to phenanthroline or dipyridyl but differing in having other groups attached either to the pyridin or benzene part of the molecule when prepared will be found to form metallic complexes in the same manner that these two compounds do. It is impossible to foretell the effect which substitution might have on the stability, normal oxidation potential and the other properties which make possible the excellent results obtained with the ferrous phenanthroline complex. So far as is known, this is the first attempt to use compounds of the metallic ammine type as indicators. The success which has been attained in this case with ferrous phenanthroline sulfate should be an incentive to investigation of related compounds.

SUMMARY

1. It has been shown that the ferrous o-phenanthroline complex ion has the properties of an ideal indicator for use with powerful oxidants. It has a high normal oxidation potential, high effective oxidation potential, is reversible and mobile and undergoes a vivid and intense color change.

2. When it is used as the indicator in titrations of ferrous sulfate with either potassium dichromate or ceric sulfate or the reverse titrations, a high degree of precision is possible.

3. Accurate results are obtained when it is used in the standardization of ferrous sulfate solutions with potassium dichromate.

4. By means of it two methods of standardizing ceric sulfate solutions are available: (a) Against potassium dichromate through ferrous sulfate; (b) Against sodium oxalate by adding excess ceric sulfate and titrating excess with ferrous sulfate.

5. Potassium dichromate and ceric sulfate solutions are thus available for titrations of high precision without the use of the potentiometer.

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